In the Application of:

VINAY G. SAKHRANI, ET AL.	DOCKET NO.: 5764-001
APPLICATION NO.: 10/791,542	GROUP ART UNIT: 1773
FILED: MARCH 2, 2004	EXAMINER: RAMSEY ZACHARIA

FOR: ARTICLE WITH LUBRICATED SURFACE AND METHOD

DECLARATION OF VINAY G. SAKHRANI PURSUANT TO 37 C.F.R. § 1.132

I hereby declare as follows:

1. I am the same Vinay G. Sakhrani who is a named co-inventor of Application No. 10/791,542.

2. I am a graduate of North Carolina State University with a Masters of Science degree and a background in polymer materials, plasma science, and plasma assisted CVD coatings.

3. I am employed by TriboFilm Research, Inc. as Vice-President of Technology.

4. In the Final Office Action mailed on March 21, 2008 for the above-referenced application, the Examiner rejected all of the pending claims under 37 C.F.R. 103(a) as being unpatentable over U.S. Patent No. 4,822,632 (hereinafter Williams) in view of U.S. Patent No. 5,830,577 (hereinafter Murayama). The Examiner appears to base his rejection, in whole or in part, on the assertion that silicone oil and perfluoropolyethers are interchangeable with one another for use as lubricants based on the teachings of Murayama; that the perfluoropolyether of Murayama can be substituted for the silicone oil of Williams; and that the teaching of "any pressure" in relation to the pressure at which the plasma is generated encompasses the extreme vacuum conditions of Williams as well as the atmospheric pressure conditions of the above-referenced application. However, these assertions by the Examiner are incorrect.

To obtain a better appreciation for the differences between the present application and the teachings of Williams and Murayama, as well as the

unexpected results and advantages flowing therefrom, the Examiner is directed to paragraph 6 below.

5. The following experiments were carried out by me or under my direct supervision and control to demonstrate the advantages of the present application. Specifically, the following data demonstrate the advantageous properties obtained through the following differences in the teachings of Williams and Murayama and the teachings of the present application: the use of a perfluoropolyether lubricant exposed to an energy source, such as an ionizing gas plasma at atmospheric pressure, and not a silicone-based lubricant exposed to an ionizing gas plasma at extreme vacuum. Experiments H, I, J, K, M, and N are new experiments that were conducted comparing vacuum and plasma technology treatments for both silicone oil and PFPE where all plasma conditions including power, treatment time, and plasma gas were kept constant. The only varying parameter was pressure. Experiments A, C, and D are comparative experiments and do not represent embodiments of the present application. Experiments B, E, and L are embodiments of the present application, and Experiments F, G, H, I, J, K, M, and N include embodiments of the present application as well as comparative examples.

<u>Comparative Experiment A (Figure 1)</u>

Syringes Prepared According to Example 2 of the Williams Patent

10cc polypropylene syringes barrels were coated with a 5 percent solvent solution of polydimethylsiloxane by dipping. The syringe barrels were allowed to dry at ambient conditions to evaporate the solvent. The syringe barrels were then exposed to an energy source, in this case a vacuum air plasma at the following conditions:

- Pressure in the plasma chamber – 300 millitorr
- Power – 125 watts
- Time of exposure to the plasma – 10 minutes

The syringe barrels were then assembled with unlubricated halobutyl rubber stoppers. The assembled syringes were then placed in a Harvard Apparatus syringe pump, and the force exerted by the syringe pump on the assembled

syringe (that is, the force required to move the stopper in the syringe barrel) was measured using a Dillon AFG-100N digital force gauge. The travel speed was about 10 ml/min (the speed of 10 ml/min was selected to best demonstrate stick-slip phenomenon because higher speeds tend to mask the phenomenon).

Figure 1 presents the results of this experiment. A very large force was required to initiate movement of the stopper (break-free force). The force required to maintain movement steadily increased until the force limit of the syringe pump was reached. This indicated that the lubricant was over-crosslinked causing a complete loss of its lubricating characteristics.

Experiment B (Figure 2)

Syringes Prepared According to Applicants' Present Application

10 cc polypropylene syringe barrels were spray coated with a linear perfluoropolyether lubricant without reactive functional groups and exposed to an energy source, in this case an ionizing gas plasma at about atmospheric pressure at the following conditions:

- Pressure in the plasma chamber – atmospheric pressure
- Plasma gas – helium
- Power – about 100 watts
- Time of exposure to the plasma – 0.5 second

The syringes were then assembled with unlubricated halobutyl rubber stoppers and tested on the same equipment used for Experiment A. Figure 2 (Experiment B) presents the results of this experiment and shows that only a very small break-free force was required to initiate movement, and that a minimal force was required to maintain movement (about 1/20th of the force required for the syringes treated according to the Williams teachings in Experiment A).

Comparative Experiment C (Figure 2)

Comparison with Perfluoropolyether Lubricant Exposed to Vacuum Plasma

In order to demonstrate the difference between using vacuum plasma technology (Williams) as the energy source and atmospheric pressure plasma technology (present application) as the energy source, 10 cc polypropylene syringe barrels coated with the perfluorpolyether lubricant were exposed to the vacuum plasma according to the parameters of Experiment A (that is, the Williams patent). These syringe barrels were then assembled with unlubricated halobutyl rubber stoppers and tested with the same apparatus as described above. The results are shown in Figure 2 (Comparative Experiment C). While these syringes exhibited a low initial break-free force, the force needed to maintain movement steadily increased until the upper limit of the force gauge was reached. This indicated that the perfluoropolyether lubricant was over-crosslinked causing a loss of its lubricating characteristics.

Comparative Experiment D (Figure 2)

Comparison with Perfluoropolyether Lubricant Not Exposed to an Energy Source

As a comparative example, 10cc polypropylene syringe barrels were coated with the perfluoropolyether lubricant and were NOT exposed to an energy source. The lubricated barrels were then assembled with unlubricated halobutyl rubber stoppers and tested with the same apparatus as described above. The results are shown in Figure 2 (Comparative Experiment D). The syringes exhibited extreme stick-slip phenomenon where the stopper would alternately stick then suddenly move. This stick-slip phenomenon is due to lubricant migration from the barrel/stopper interface and is also observed in commercially available silicone lubricated syringes.

Experiment E (Figure 3)
Plasma Treatment Prior to Application of the Lubricant

Uncoated 1ml glass syringe barrels were treated with a helium plasma at about atmospheric pressure according to the present application at the following conditions:

- Pressure in the plasma chamber – atmospheric pressure
- Plasma gas – helium
- Power – about 100 watts
- Time of exposure to the plasma – 3 seconds

The syringe barrels were then lubricated with Fomblin ZDOL followed by heating for 5 minutes to about 250°C. Fomblin ZDOL is a functionalized perfluoropolyether (PFPE) with hydroxyl (-OH) functional groups at both ends of the PFPE molecule. The syringes were then assembled with halobutyl rubber stoppers and tested on the same equipment used for Experiment A. Figure 3 (Experiment E) presents the results of this experiment and shows that only a small break-free force was required to initiate movement, and minimal force was required to maintain movement without any stick-slip behavior.

Experiment F (Figure 4)
Mixtures of Perfluoropolyethers with and without Functional Groups (Binding Sites). Comparison of Plasma Treatment Using Extreme Vacuum and Atmospheric Pressure Plasma Technologies

In order to demonstrate the difference between using vacuum plasma technology as the energy source and atmospheric pressure plasma technology as the energy source, 12ml polypropylene syringe barrels were lubricated with a 50-50 mixture of Fomblin M (inert PFPE without functional end-groups) and Fomblin ZDOL (di-hydroxyl terminated PFPE, a lubricant with a binding site as in Murayama).

One set of syringe barrels was treated with a helium plasma at about atmospheric pressure using the same parameters listed above for Experiment B (the present application). The second set of syringe barrels was treated with an air

plasma under vacuum conditions according to parameters of Experiment A (Example 2 of the Williams patent). Both set of syringes were assembled with unlubricated polyisoprene stoppers and tested with the same apparatus as described in Experiment A. Figure 4 presents the results of this experiment and shows that the syringes treated using atmospheric pressure plasma technology exhibited a low initial break-free force (about 1 pound of force) followed by minimal force to maintain movement without any stick-slip behavior. In comparison, syringes treated using vacuum plasma technology per Williams' teachings required about 8 pounds of force to initiate movement followed by continuously increasing force to maintain movement of the syringe stopper until the upper limit of the force gauge was reached. This indicated that the perfluoropolyether lubricant was over-crosslinked under vacuum plasma conditions causing a loss of its lubricating characteristics.

Experiment G (Figure 5)
Comparison of Plasma at Extreme Vacuum and Atmospheric Pressure

In order to demonstrate the difference between using vacuum plasma technology as the energy source and atmospheric pressure plasma technology as the energy source, 12ml polypropylene syringe barrels were lubricated with Fomblin Y (inert branched PFPE without functional end-groups).

One set of syringe barrels was treated with a helium plasma at about atmospheric pressure using the same parameters listed above for Experiment B (the present application). The second set of syringe barrels was treated with an air plasma under vacuum conditions according to the parameters of Experiment A (Example 2 of the Williams patent). Both set of syringes were assembled with unlubricated polyisoprene stoppers and tested with the same apparatus as described in Experiment A. Figure 5 presents the results of this experiment and shows that the syringes treated with atmospheric pressure plasma exhibited a low initial break-free force (about 2.2 pounds of force) followed by minimal force to maintain movement without any stick-slip behavior. In comparison, syringes treated with vacuum plasma per Williams' teachings required about 13 pounds of force to initiate movement followed by continuously increasing force to maintain

movement of the syringe stopper until the upper limit of the force gauge was reached. This indicated that the perfluoropolyether lubricant was over-crosslinked under vacuum plasma conditions causing a loss of its lubricating characteristics.

Experiment H (Figure 6)

Comparison Between Vacuum Plasma at Different Power Levels Using Silicone Lubricant

In order to demonstrate the difference between using vacuum plasma technology as the energy source operated at the power level disclosed by Williams (125 watts) and the power level disclosed by the present application for atmospheric pressure plasma technology (about 100 watts), 10ml polypropylene syringes were lubricated with silicone oil as used in the Williams patent. A 1.5% solution by weight of silicone oil (Dow Corning 1000cst) in hexane was prepared and the syringes were coated with the solution as described in Williams Example 2. The only change from Williams was the use of hexane as a solvent rather than using Freon due to current unavailability of Freon. The 2 minute exposure time is within the range taught by Williams. The solvent was allowed to evaporate and then the syringes were exposed to the vacuum plasma at the following conditions:

- Pressure in the plasma chamber – 300 millitorr
- Plasma gas – helium
- Power – Experiment 1: 125 watts as per Williams
  Experiment 2: about 100 watts to duplicate power used for atmospheric plasma in the present application
- Time of exposure to the plasma – 2 minutes

The syringes were assembled with unlubricated polyisoprene stoppers and tested on the same equipment used for Experiment A. Figure 6 presents the results of this experiment and shows that a large force was required to initiate initial movement of the stopper (break-free force). The force required to maintain movement either remained at the break-free level or steadily increased until the force limit of the syringe pump was reached. As a control, Figure 6 also includes a graph of a syringe coated with the same silicone, but not exposed to vacuum

plasma. The control showed a significantly lower break-free force but also exhibited extreme stick-slip phenomena. This experiment demonstrated that vacuum plasma technology at the power level of Williams and at the power level of the present application significantly reduced the lubricity of silicone oil.

Experiment I (Figure 7)

Silicone Oil Exposed to Atmospheric Plasma

In order to demonstrate the effect of treating silicone oil using atmospheric plasma technology, 10 ml polypropylene syringes were coated with silicone oil and exposed to atmospheric plasma at the following conditions:

- Pressure in the plasma chamber – about atmospheric pressure
- Plasma gas – helium
- Power – about 100 watts
- Time of exposure to plasma – 2 minutes

The 2 minute exposure time is within the range taught by Williams. The syringes were then assembled with unlubricated polyisoprene stoppers and tested on the same equipment used for Experiment A. Figure 7 present the results of this experiment and shows a very low break-free force and a minimal force needed to continue movement. The control had a break-free force approximately three times higher and exhibited extreme stick-slip phenomenon. This experiment demonstrated the beneficial effect of atmospheric plasma technology, even when using silicone oil as the lubricant (compare these results to Experiment H which exposed silicone oil to vacuum plasma).

Experiment J (Figure 8)

Comparison between Vacuum Plasma at Different Power Levels Using Perfluoropolyether Lubricant

In order to demonstrate the difference between using vacuum plasma technology as the energy source operated at the power level disclosed by Williams (125 watts) and the power level disclosed by the present application for

atmospheric pressure plasma technology (about 100 watts), 10ml polypropylene syringes were lubricated with 1.5 microliter of PFPE lubricant (Fomblin M100). The solvent was allowed to evaporate and then the syringes were exposed to the vacuum plasma at the following conditions:

- Pressure in the plasma chamber – 300 millitorr
- Plasma gas – helium
- Power – Experiment 1: 125 watts as per Williams
  Experiment 2: about 100 watts to duplicate power used for atmospheric plasma in the present application
- Time of exposure to the plasma – 2 minutes

The 2 minute exposure time is within the range taught by Williams. The syringes were then assembled with unlubricated polyisoprene stoppers and tested on the same equipment used for Experiment A. Figure 8 present the results of this experiment and shows that both syringes treated using vacuum plasma technology required steadily increasing force to maintain movement of the stoppers until the upper limit of the force gauge was reached. As a control, Figure 8 also includes the results from a syringe coated with the PFPE lubricant but not exposed to the vacuum plasma. The graph of the control shows an initial break-free force, then extreme stick-slip phenomenon. Significantly, even though the control exhibited stick-slip, the force required to maintain movement of the stopper was about 2-3 pounds, while the syringes treated using vacuum plasma technology required about 20 pounds of force to maintain even a small amount of movement.

Experiment K (Figure 9)

Perfluoropolyether Lubricant and Atmospheric Plasma Using Plasma Treatment Time of Williams

In order to demonstrate the effect of operating the atmospheric plasma as taught in the present application at the treatment time disclosed by Williams, 10 ml polypropylene syringes were coated with PFPE lubricant (Fomblin M100) and exposed to atmospheric plasma at the following conditions:

- Pressure in the plasma chamber – about atmospheric pressure
- Plasma gas – helium
- Power – about 100 watts
- Time of exposure to plasma – 2 minutes

The 2 minute exposure time is within the range taught by Williams. The syringes were then assembled with unlubricated polyisoprene stoppers and tested on the same equipment used for Experiment A. Figure 9 present the results of this experiment and shows that the syringe treated using atmospheric pressure plasma technology exhibited an extremely low break-free force, and an even lower force to maintain continued movement of the stopper (both forces were less than 1 pound). Thus, the same beneficial results are seen even with the extended exposure time taught by Williams.

Experiment L (Figure 10)

Perfluoropolyether Lubricant and Gamma Radiation

In order to demonstrate the effect of using gamma radiation as the energy source, 10 ml polypropylene syringes were coated with PFPE lubricant (Fomblin M100) and exposed to a gamma radiation dose of approximately 33 kGy. The syringes were then assembled with unlubricated butyl rubber stoppers and tested on the same equipment used for Experiment A. Figure 10 present the results of this experiment and shows that the gamma radiation treated syringe exhibited an extremely low break-free force, and an even lower force to maintain continued movement of the stopper (both forces were less than 1 pound). These results are essentially the same as that achieved using atmospheric pressure plasma technology.

Experiment M (Figure 11)

Comparison of Vacuum and Atmospheric Pressure Plasma Technologies for Pre- and Post-Treatment Using Silicone Oil

In order to demonstrate the effect of using vacuum plasma technology and atmospheric pressure plasma technology for both pre-treatment of the syringe prior to applying the lubricant and post-treatment of the syringe after applying the lubricant, two sets of syringes were prepared. The first set was exposed to vacuum plasma for the pre- and post-treatment. Silicone oil was applied to the syringe after the pre-treatment and before the post-treatment. The vacuum plasma conditions for both pre- and post-treatment were as follows:

- Pressure in the plasma chamber – 300 millitorr
- Plasma gas – helium
- Power – 100 watts as per the range specified in Williams
- Time of exposure to the plasma – 2 minutes

The second set of syringes was exposed to atmospheric plasma for the pre- and post-treatment. Silicone oil was applied to the syringe after the pre-treatment and before the post-treatment. The atmospheric plasma conditions for both pre- and post-treatment were as follows:

- Pressure in the plasma chamber – about atmospheric pressure
- Plasma gas – helium
- Power – about 100 watts
- Time of exposure to plasma – 2 minutes

The syringes were then assembled with unlubricated polyisoprene stoppers and tested on the same equipment used for Experiment A. Figure 11 present the results of this experiment and shows that the syringe treated using vacuum plasma technology required steadily increasing force to maintain movement of the stopper and peaked at about 20 pounds. The force dropped quickly to about 10 pounds, then decreased to about 7 pounds for continued movement. In contrast, the syringe treated using atmospheric pressure plasma technology exhibited a break-

free force of about 2-3 pounds, then a steady force of about 1 pound for continued movement. Thus, the atmospheric plasma pre- and post-treatment provided significantly better results than vacuum plasma pre-and post-treatment.

Experiment N (Figure 12)

Comparison of Vacuum and Atmospheric Plasma for Pre- and Post-Treatment Using Perfluoropolyethylene

This experiment duplicates Experiment M except that a PFPE lubricant (Fomblin M100) was in place of silicone oil. Figure 12 present the results of this experiment and shows that the syringe treated using vacuum plasma technology required steadily increasing force to maintain movement of the stopper and peaked at about 13 pounds. The force dropped quickly to about 3 pounds, then slowly increased again. In contrast, the syringe treated using atmospheric pressure plasma technology exhibited a break-free force of less than 1 pound, then an even lower steady force for continued movement. Thus, the atmospheric plasma pre- and post-treatment provided significantly better results than vacuum plasma pre- and post-treatment.

Conclusions

- The results of Experiments A-N indicate that atmospheric plasma produces a significant and unexpected beneficial effect over vacuum plasma as taught by Williams when all variables other than pressure are held constant. Thus, the statement in Williams that the process may be carried out at "any pressure" is incorrect.
- The results of Experiment A indicate that beneficial results using the teachings of the Williams patent with silicone oil could not be obtained. Results of Experiment A were similar to Experiment C in which the method of the Williams patent (vacuum plasma technology) was used with the lubricant of the present application.
- The results of Experiment D indicate that poor results are obtained when using the perfluoropolyether lubricant without any plasma treatment. These results indicate that the beneficial results cannot be obtained by the lubricant alone.
- The results of Experiments B indicate that excellent results were achieved with the methods of the present application for linear perfluoropolyethers without reactive functional groups, and the results of Experiment G indicate similar results for branched perfluoropolyethers without reactive functional groups.
- The results of Experiment F, in which a mixture of a lubricant without functional end groups (binding sites) and a lubricant with functional binding sites indicate that the lubricant of Murayama does not work using the teachings of Williams for vacuum plasma technology. However, the same lubricant mixture when treated using atmospheric pressure plasma technology results in superior syringe performance.
- The results of Experiment E indicate that pretreating the surface using atmospheric pressure plasma technology has beneficial results.
- The results of Experiment H indicate that there is little difference in the results obtained when the vacuum plasma process as taught by Williams is operated at power levels of 100 and 125 watts. A power level of 100 watts corresponds to the maximum power level of the atmospheric plasma process that could be used without causing undesirable arcing inside the syringe, and a power level of 125 watts corresponds to the power level used in the examples in Williams.

- The results of Experiment I indicate that the beneficial effects of atmospheric pressure plasma technology are obtained when using silicone as the lubricant.
- The results of Experiment J indicate that poor results are obtained using PFPE lubricant and vacuum plasma technology power levels of both 100 and 125 watts.
- The results of Experiment K indicate that the treatment using atmospheric pressure plasma technology is equally effective at the longer exposure time (2 minutes) of Williams.
- The results of Experiment L indicate that results comparable to atmospheric pressure plasma technology are obtained when the PFPE lubricant is exposed to gamma radiation.
- The results of Experiments M and N indicate that the combination of pre-treat and post-treat using atmospheric pressure plasma technology has a beneficial effect with both silicone oil and PFPE as the lubricant, but no beneficial effect is seen when vacuum plasma technology is used for pre-treat and post-treat.

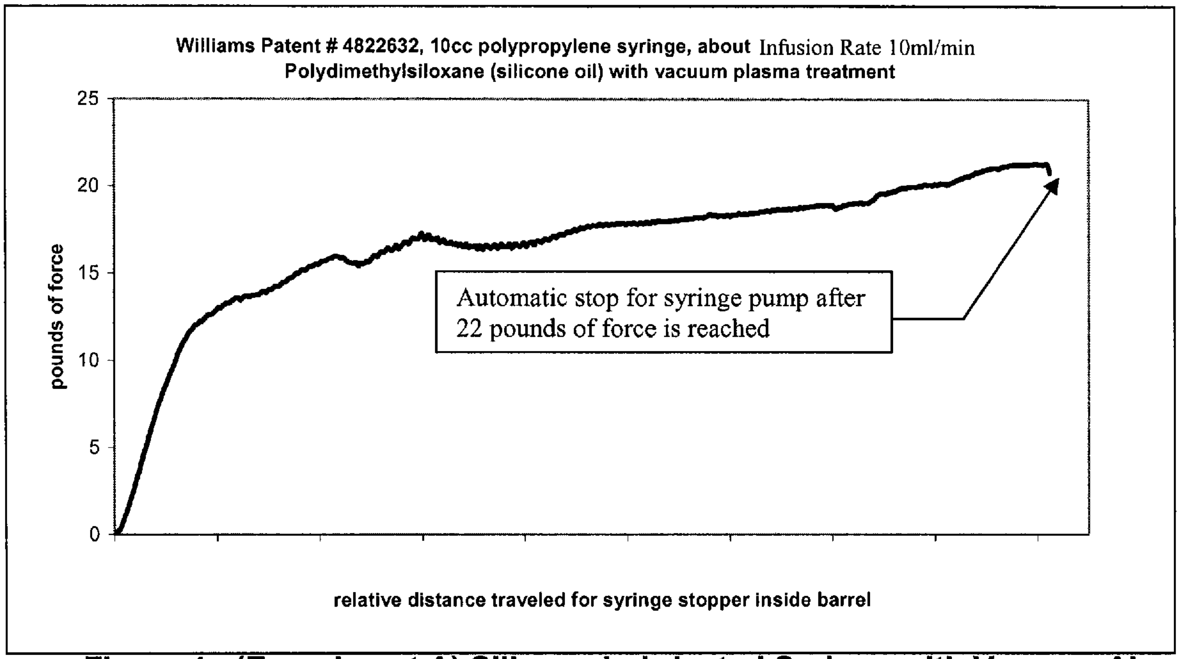

Figure 1. (Experiment A) Silicone Lubricated Syringe with Vacuum Air Plasma Treatment According to Williams et al. (U.S. Patent No. 4,822,632)

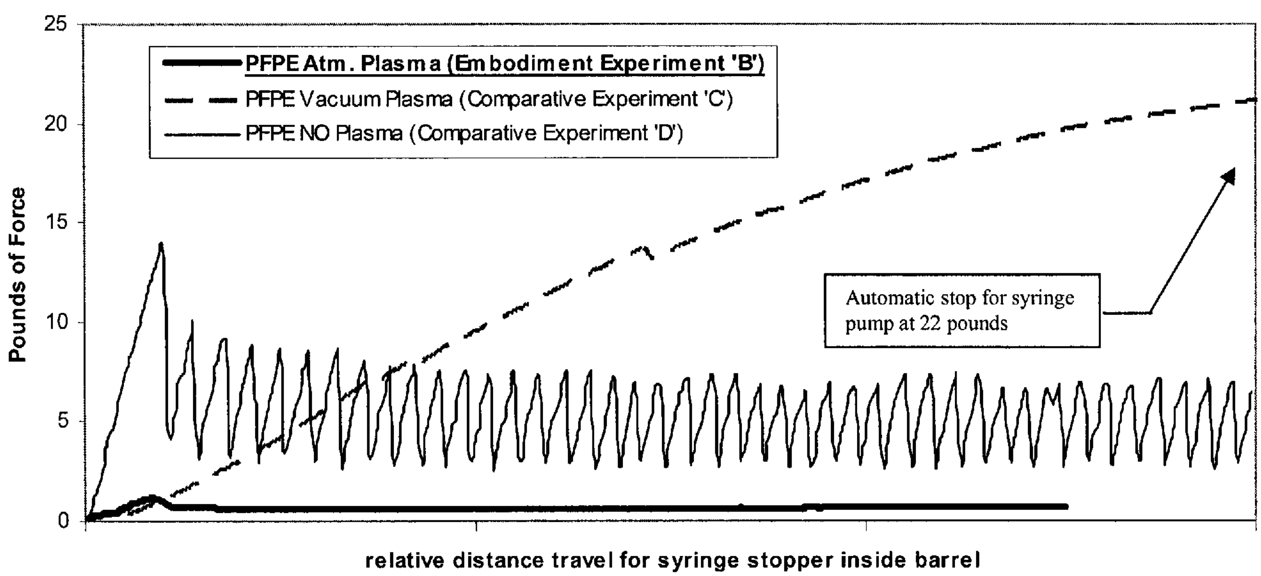

Figure 2. (Experiments B, C, and D) Influence of Plasma Treatments on Perfluoropolyether (PFPE).
Embodiment "Experiment B" – PFPE with Atmospheric Plasma
Comparative Example "Experiment C" – PFPE with Vacuum Plasma
Comparative Example "Experiment D" – PFPE without Plasma Treatment

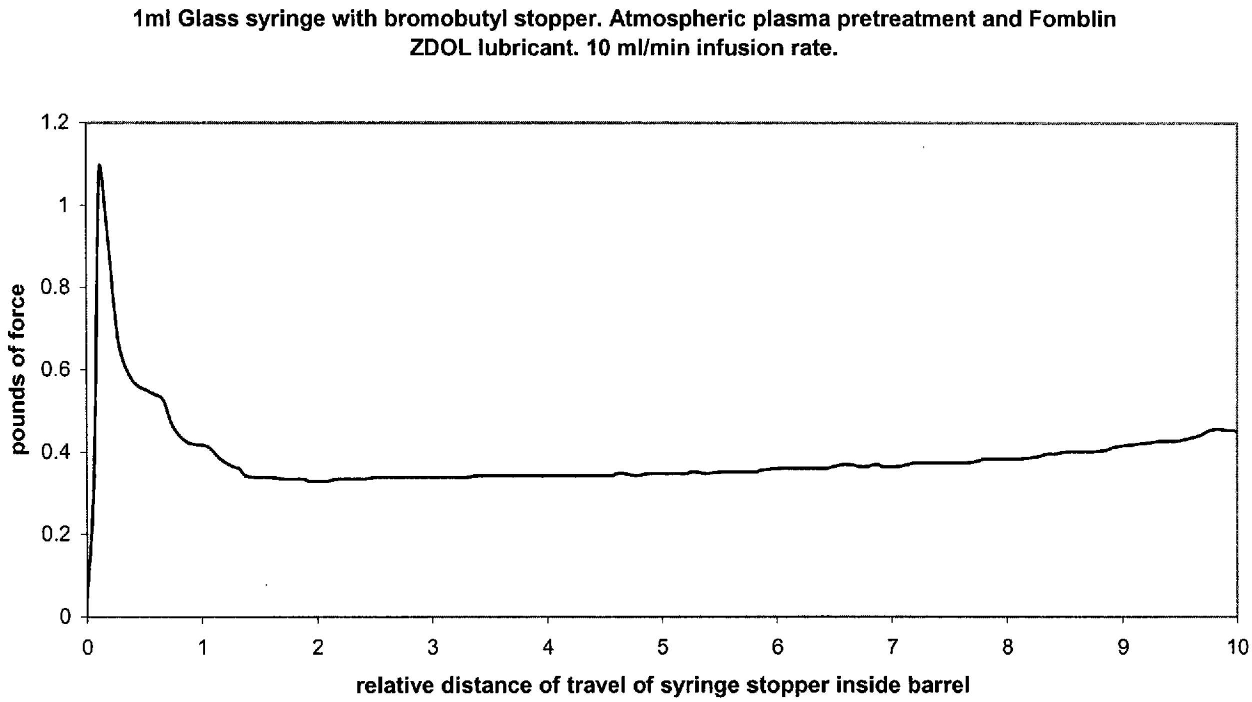

Figure 3. (Experiment E) Fomblin ZDOL (di-hydroxyl terminated liner PFPE). Atmospheric Plasma Treatment Only.

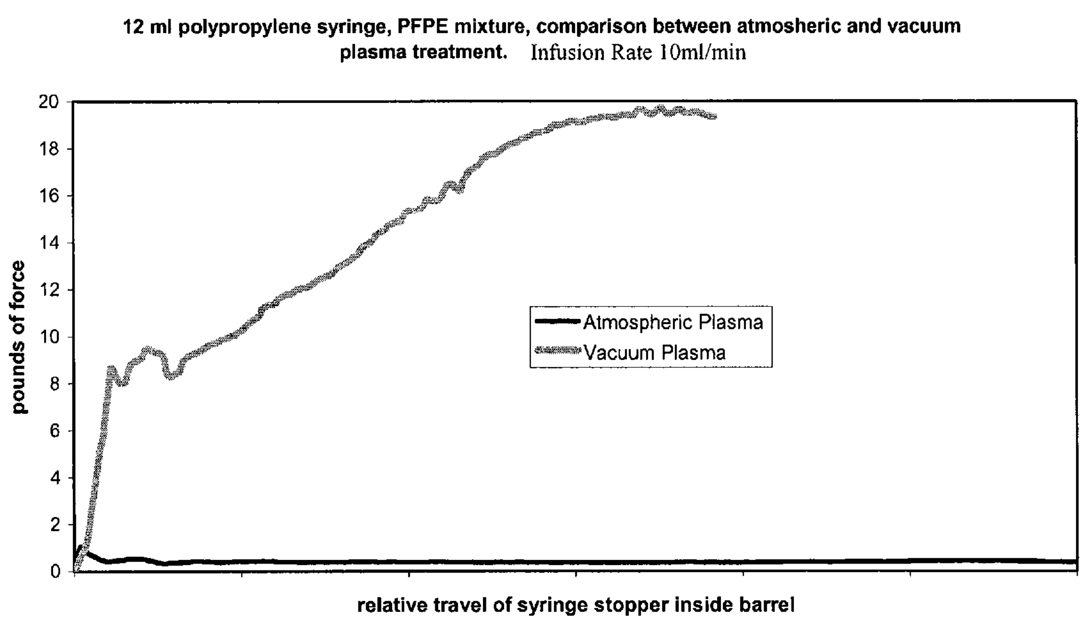

Figure 4: (Experiment F) 50/50 mixture of Fomblin M 60 (inert linear PFPE) and Fomblin ZDOL (di-hydroxyl terminated linear PFPE). Atmospheric and Vacuum plasma comparison.

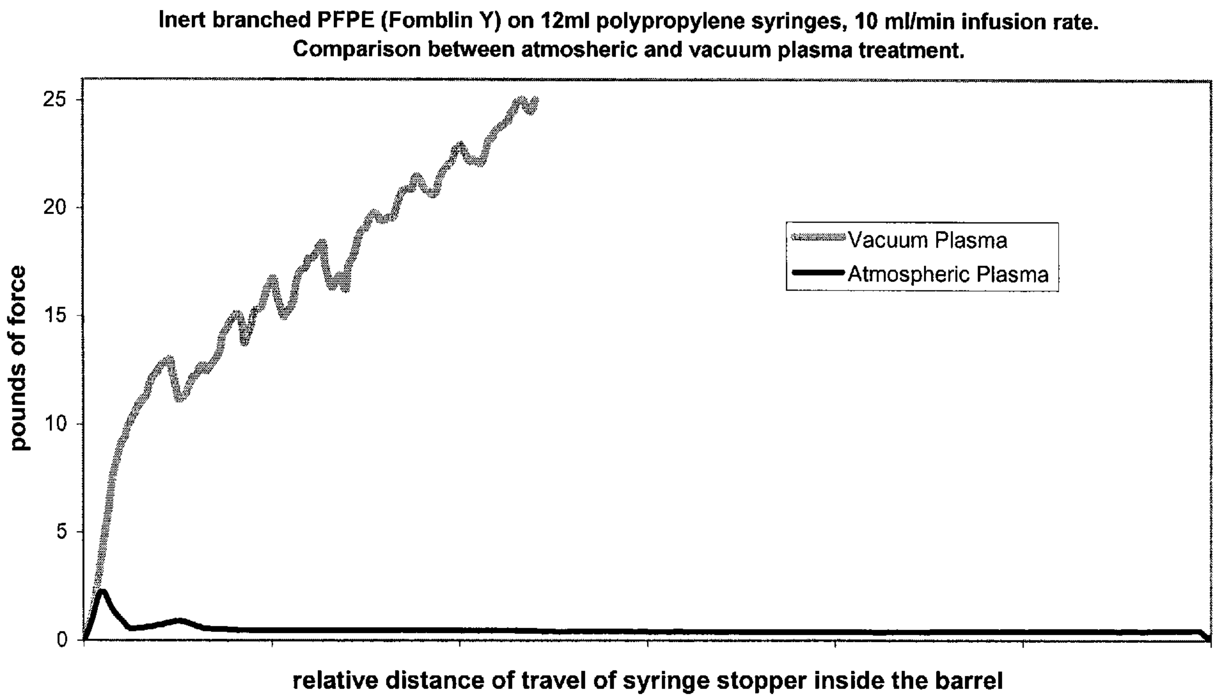

Figure 5: (Experiment G) Inert Branched PFPE Lubricant Fomblin Y. Atmospheric and Vacuum Plasma Comparison.

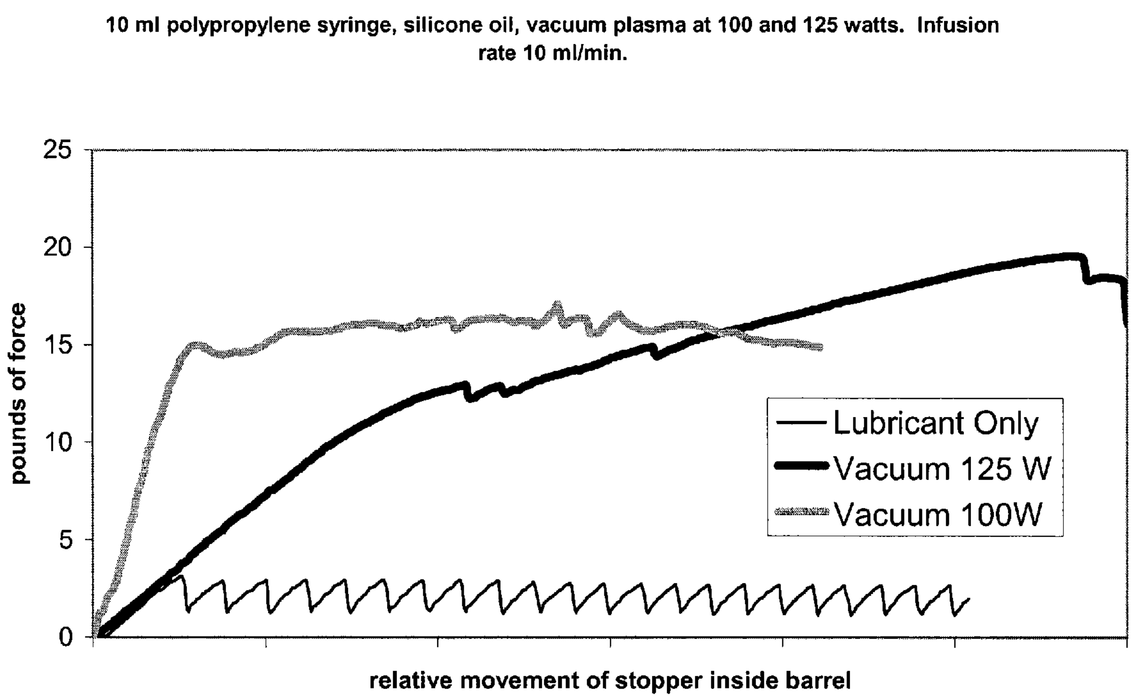

Figure 6: (Experiment H) Syringe Lubricated with Silicone Oil. Vacuum Plasma at 100 and 125 Watts.

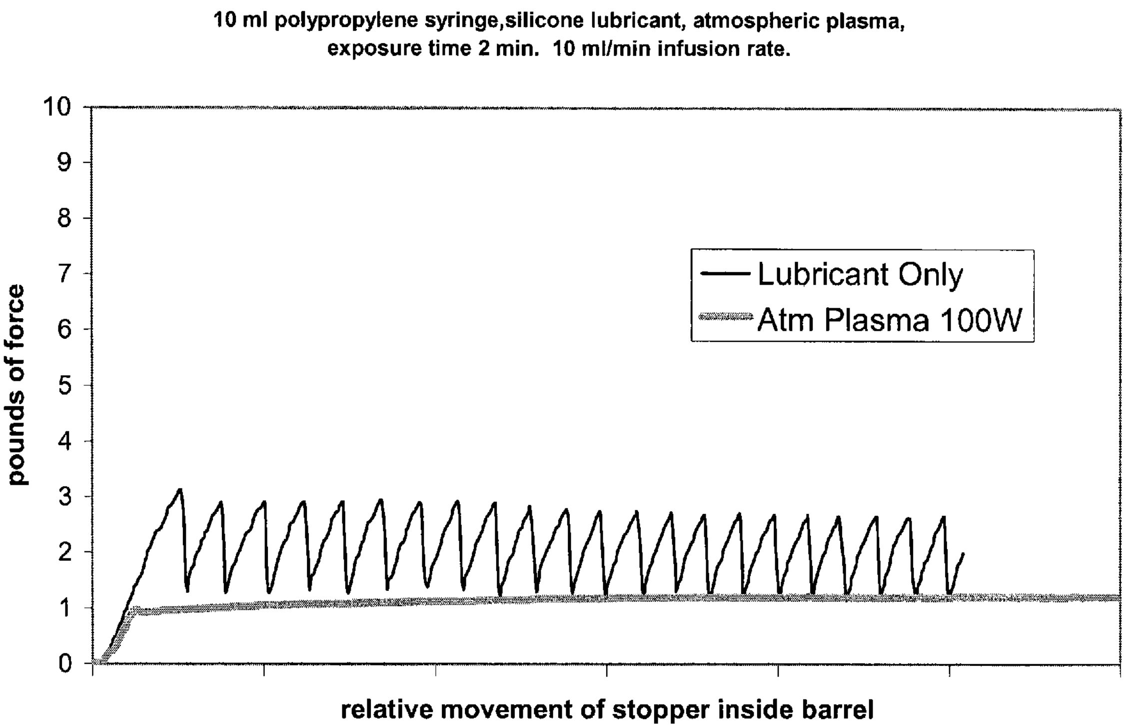

Figure 7: (Experiment I) Silicone Oil Lubricant and Atmospheric Plasma

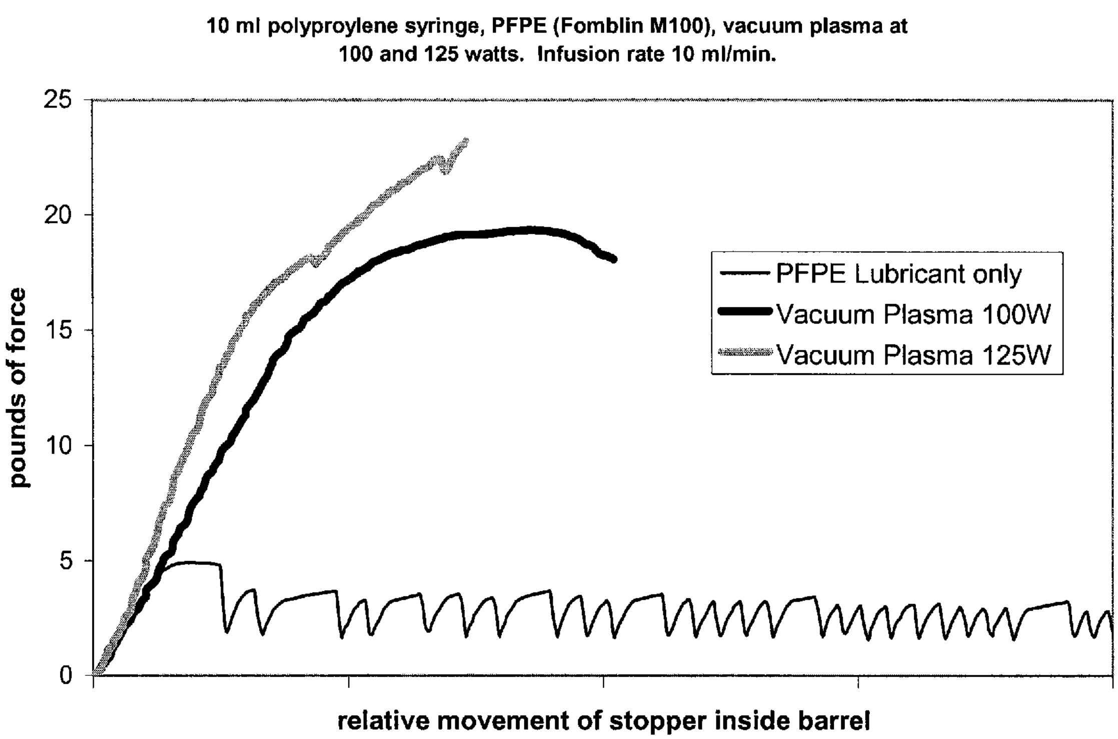

Figure 8: (Experiment J) Syringe Lubricated with PFPE. Vacuum Plasma at 100 and 125 Watts.

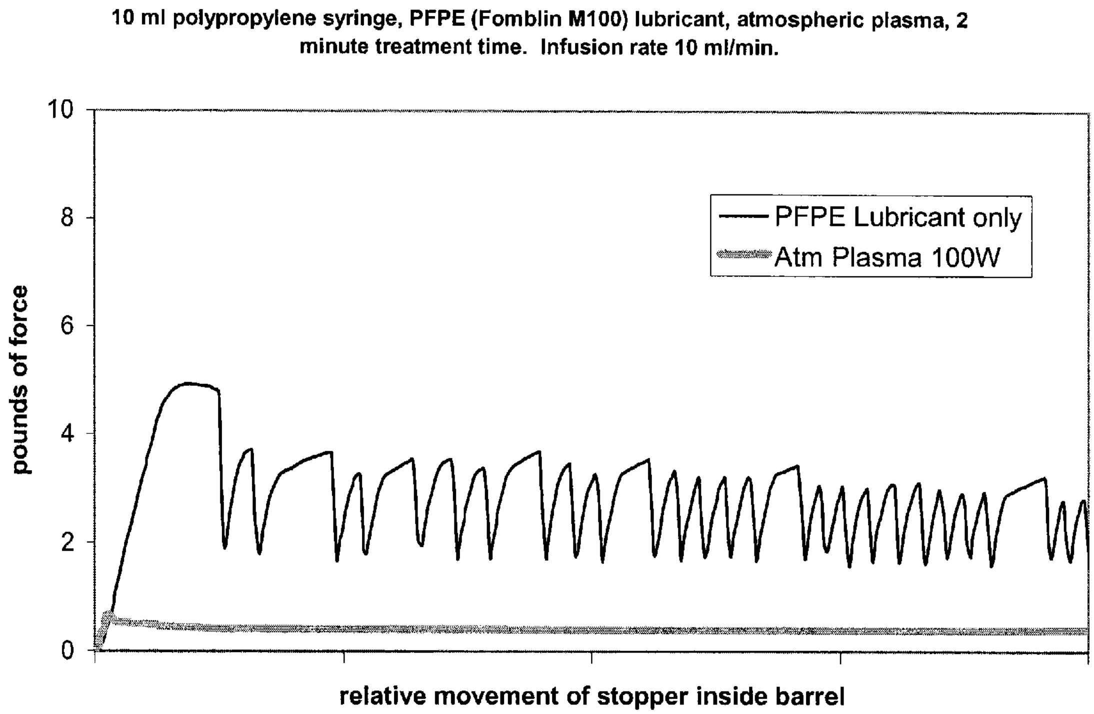

Figure 9: (Experiment K) Syringe Lubricated with PFPE. Vacuum Plasma, 2 Minute Treatment Time.

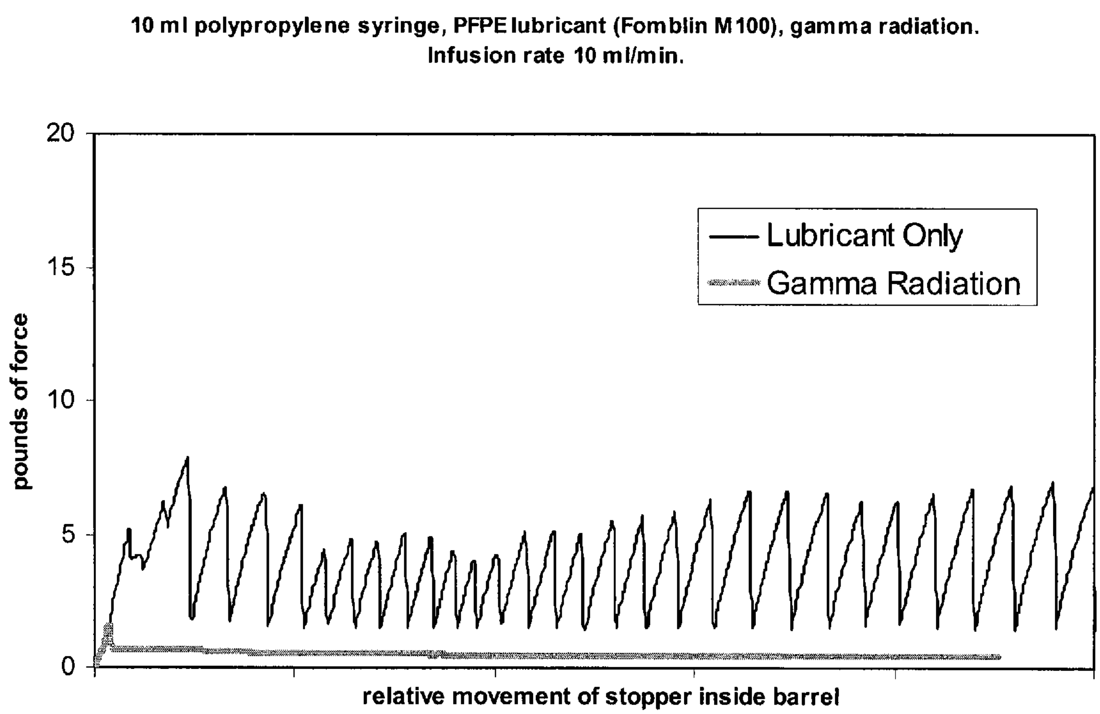

Figure 10: (Experiment L) Syringe Lubricated with PFPE. Gamma Radiation.

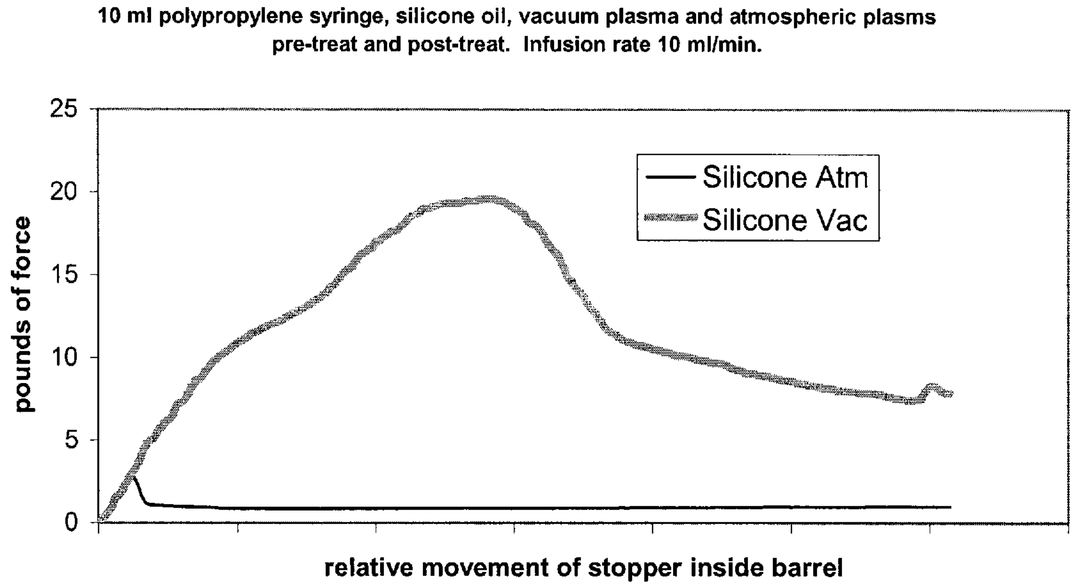

Figure 11: (Experiment M) Syringe Lubricated with Silicone Oil. Vacuum Plasma and Atmospheric Plasma Pre-Treat and Post-Treat

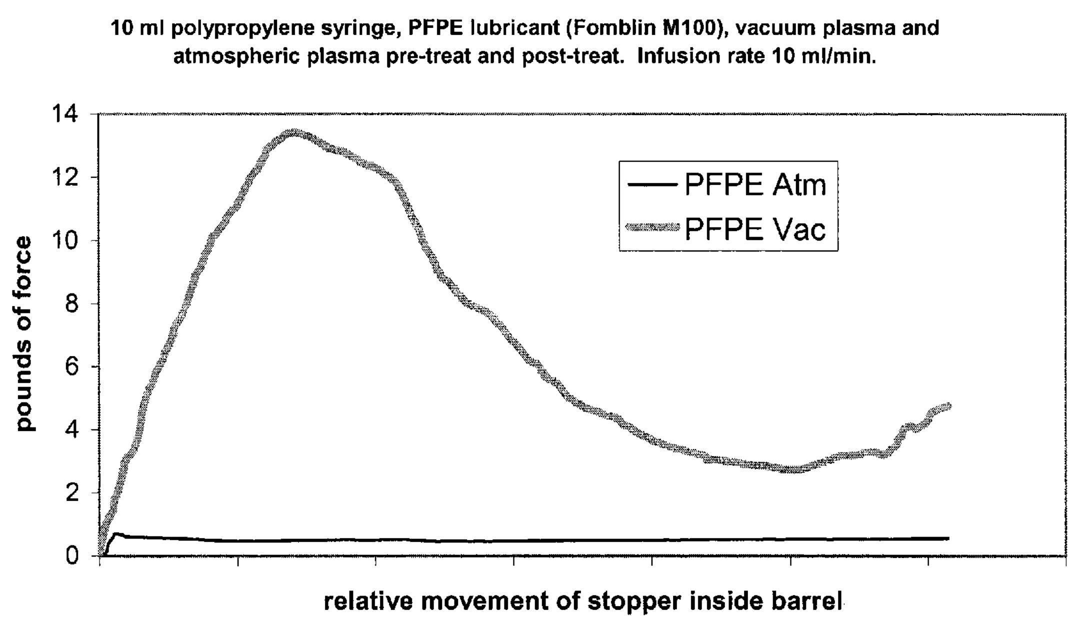

Figure 12: (Experiment N) Syringe Lubricated with PFPE. Vacuum Plasma and Atmospheric Plasma Pre-Treat and Post-Treat

6. Results

The results show that the difference in performance between the syringes prepared according to the present application compared to those prepared by the Williams teachings provides unexpected and surprising results. It is clear from these results that the product obtained by the present application is significantly different than that produced according to the Williams teachings, and that the difference is due to atmospheric pressure plasma technology versus vacuum plasma technology. The experimentation confirms that when all other parameters are held constant, the significantly different results are caused by the effects produced by plasma generated at about atmospheric pressure rather than a plasma generated under conditions of extreme vacuum.

The results obtained from the above experiments prove that the Examiner's assertion that Williams and Murayama can be combined is incorrect. First, Williams does not produce a level of lubricity comparable to that obtained by the present application. Second, substituting the perfluoropolyether of the present application into the method of Williams produces poor results. If the teachings of Williams and Murayama are combinable as asserted by the Examiner, then the results of Experiment C should have been comparable to the results of Experiment B. Third, substituting a perfluoropolyether with or without binding sites into the method of Williams also produces poor results. Once again, if the teachings of Williams and Murayama are combinable, then the results of Experiment F using vacuum plasma technology should have been comparable to the results of Experiment B using atmospheric pressure plasma technology.

Finally, the experimentation showed that Williams fails to teach that its process may be carried out at any pressure. Murayama does not teach wholesale substitution of silicone oils and perfluoropolyethers without a host compound.

7. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing therefrom.

Vinay Sakhrani

Vinay G. Sakhrani

May 13, 2008

Date